values observed for reaction 8 suggests strongly that a common intermediate is precursor to stable Co^{III} products in both the photochemical systems and in reaction 8. We feel the most logical candidate for this intermediate is the coordinatively unsaturated Co^{III} ammine $[Co(NH_3)_5]^{3+}$, obtained in the photochemical systems from $[Co(NH_3)_5(O_2)]^{3+}$ and in reaction 8 from either $[Co(NH_3)_5(N_2)]^{3+}$ or $[Co(NH_3)_5(NNNNO)]^{3+}$. In neither the photochemical systems nor reaction 8 is it likely that the original reactants (i.e., 2 or [Co-$(NH_3)_5(N_3)]^{2+}$) are immediate precursors to [Co-$(NH_3)_5]^{3+}$. The five-coordinate intermediate can be expected to react with its solvation sphere at a rate at least competitive with reorganization of that solvation sphere. Consequently, $[Co(NH_3)_5]^{3+}$ produced directly from 2 or its excited states (i.e., before the reduced Co center departed) would react with a solvation sphere appropriate to a species having a charge of 4+, while $[Co(NH_3)_5]^{3+}$ produced directly from $[Co(NH_3)_5(N_3)]^{3+}$ after reaction with NO^+ would react with a solvation sphere appropriate to a species having a charge of 2+ or 3+. Since anion incorporation is well known to depend on the charge of the incorporating species,[44] it is highly unlikely that k_X/k_W values obtained for photochemical systems and for reaction 8 could be in agreement as close as that observed unless the precursor to $[Co(NH_3)_5]^{3+}$ in both cases had the same charge. It has already been pointed out[32] that species such as $[Co(NH_3)_5(N_2)]^{3+}$ or $[Co(NH_3)_5(NNNNO)]^{3+}$,

with lifetimes long compared to the time required for solvent reorganization, probably are formed in reaction 8. There is no evident reason why a $[Co(NH_3)_5(O_2)]^{3+}$ complex should not have a similar lifetime.

In assessing the differences in behavior of the photochemical systems 1 + Cl^- and 2 + Cl^-, we note that Sykes has presented convincing kinetic evidence for formation of ion pairs between 1 and Cl^-.[45] For this system, Sykes found the formation constant for the ion pair to be approximately unity when the total ionic strength was 2.0. All of the anion-incorporation experiments described here were carried out with solutions having total ionic strengths considerably lower than 2.0. Under our photolysis conditions, therefore, extensive ion pairing between 1 and Cl^- probably occurs, and results obtained with 1 are expected to contain contributions from photolysis of the ion pair as well as photolysis of free 1. Our stoichiometric incorporation data allow the further conclusion that the role of Cl^- in the photochemistry of the ion pair cannot be restricted simply to promotion of formation of $[Co(NH_3)_5O_2]^{3+}$, because if this were the case the f values obtained for 1 + Cl^- would be identical with those obtained for 2 + Cl^-.

(44) For instance, see G. E. Dolbear and H. Taube, *Inorg. Chem.*, 6, 60 (1967).

(45) A. G. Sykes, *Trans. Faraday Soc.*, 59, 1334, 1343 (1963).

Oxidations of Aqueous Chromium(II). II. Chromium–Carbon Bond

Willfred Schmidt, James H. Swinehart, and Henry Taube*

Contribution from the Departments of Chemistry, Stanford University, Stanford, California 94305, and the University of California at Davis, Davis, California 95616. Received April 11, 1970

Abstract: An investigation of the formation and kinetic stability of complexes containing a chromium–carbon bond in an aqueous medium is described. Pentaaquochromium(III) ions carbon bonded to small acyclic anions such as are derived from isopropyl alcohol and diethyl ether are formed by the reduction of organic radicals with Cr(II). The organic radicals are produced by hydrogen abstraction with OH radicals. Aquation rates of the Cr(III) complexes when the organic ligands contain hydroxyl groups (alcohols) are described by the differential rate law $-d \ln [(H_2O)_5CrL^{2+}]/dt = k_1 + k_2[H^+]$. The rate laws for complexes having organic ligands which do not have a hydroxyl group (e.g., methyl or the radical derived from diethyl ether) do not show the term independent of hydrogen ion. A mechanism is proposed in which the activated complex contains a solvent molecule in a position so as to take advantage of hydrogen bonding with the organic ligand.

As part of a continuing study of oxidations of aqueous Cr(II),[1] the formation and kinetic stability of complexes formed when radicals of small acyclic molecules oxidize Cr(II) have been studied.

A recent review article[2] has covered the use of Cr(II)

as a reducing agent in a variety of organic reactions. Anet[3] first noted and isolated a stable chromium intermediate containing a chromium–carbon bond. This was the benzylchromium ion obtained in the reduction

(1) W. G. Schmidt, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 7, 1984 (1968).

(2) J. R. Hanson and E. Premuzic, *Angew. Chem., Int. Ed. Engl.*, 7, 247 (1968).

(3) F. A. L. Anet and E. LeBlanc, *J. Amer. Chem. Soc.*, 79, 2649 (1957).

of a benzyl halide by Cr(II). Additional ways of forming the benzylchromium ion and some related aralkylchromium ions were studied by Kochi and Davis.[4] The kinetics of the protonolysis of benzylchromium ion to toluene was investigated under a variety of conditions and the mechanism in an acidic buffer solution has been formulated as follows[5]

$$C_9H_6CH_2Cr^{2+} + X^- \rightleftharpoons C_9H_8CH_2CrX^+ \tag{1}$$

$$C_9H_6CH_2CrX^+ + H^+ \longrightarrow C_9H_8CH_3 + CrX^{2+} \tag{2}$$

where X^- is the anionic buffer component.

Recently the formation and aquation of a similar ion, pentaaquopyridiomethylchromium(III) has been investigated.[6,7] Reduction of simple alkyl halides with hexaaquochromium(II) has not been successful. However, it has been found that they can be reduced by ethanolamine and ethylenediamine complexes of Cr(II).[8a] In a recent paper[8b] the reduction of alkyl halides by $Cr^{II}(en)$ is described in some detail, and some properties of alkylethylenediamine–Cr(III) complexes are recorded. Chromium complexes containing carbon-bonded simple alkyl moieties have been formed (*vide infra*), but not isolated, by the reduction of hydroperoxides.[9] In this reaction an alkoxy radical is considered to be the initial product in the reduction of the hydroperoxide with Cr(II). The formation of alkoxy radicals has been postulated in the reduction of alkyl hydroperoxides by Fe(II)[10] and Cu(I).[11] These alkoxy radicals can then be further reduced to the corresponding alcohol[9] or they can undergo a β scission fragmentation in which an alkyl radical is produced. The *tert*-butoxy radical, from the reduction of *tert*-butyl hydroperoxide, fragments into acetone and a methyl radical[12]

$$(CH_3)_3CO \cdot \longrightarrow \cdot CH_3 + CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 \tag{3}$$
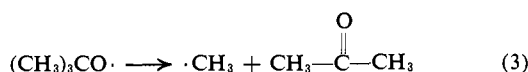
An alkylchromium ion is formed when the alkyl radical is captured by a Cr(II) ion. In the present work a series of chromium complexes containing carbon-bonded ligands have been formed by using OH radicals to abstract hydrogen atoms from organic molecules and then capturing the resulting organic radicals with aquochromium(II). The complexes formed, $(H_2O)_5$-$CrL^{2+} \equiv CrL^{2+}$, are in general more labile than Cr(III) complexes containing inorganic ligands. However, some are stable enough for isolation by ion exchange and it was possible to study the kinetics of aquation for the entire series.

(4) J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, 86, 5264 (1964).
(5) J. K. Kochi and D. Buchanan, *ibid.*, 87, 853 (1965).
(6) R. G. Coombes, M. D. Johnson, and N. Winterton, *J. Chem. Soc.*, 7029 (1965).
(7) R. G. Coombes and M. D. Johnson, *ibid., A*, 177 (1966).
(8) (a) J. K. Kochi and P. E. Mocadlo, *J. Amer. Chem. Soc.*, 88, 4094 (1966); (b) J. K. Kochi and J. W. Powers, *ibid.*, 92, 137 (1970).
(9) J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, 30, 1134 (1965).
(10) M. S. Kharasch, A. Fono, and W. Nudenberg, *ibid.*, 15, 763 (1950); 17, 207 (1952); M. S. Kharasch, F. S. Arimoto, and W. Nudenberg, *ibid.*, 16, 1556 (1951); J. W. L. Fordham and H. L. Williams, *J. Amer. Chem. Soc.*, 72, 4465 (1950); 73, 1634 (1951); R. J. Orr and H. L. Williams, *Can. J. Chem.*, 30, 985 (1952).
(11) J. K. Kochi, *Tetrahedron*, 18, 483 (1962); see, however, C. Walling and A. A. Zavitsas, *J. Amer. Chem. Soc.*, 85, 2084 (1963); J. K. Kochi, *ibid.*, 84, 2785 (1962).
(12) P. Gray, *Trans. Faraday Soc.*, 55, 760 (1959); P. Gray and A. Williams, *Chem. Rev.*, 59, 239 (1959); R. Brinton and D. Volman, *J. Chem. Phys.*, 20, 25 (1952); A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Amer. Chem. Soc.*, 78, 1190 (1956).

Experimental Section

Reagents. The following reagent grade chemicals were used without further purification: methyl alcohol, propyl alcohol, isopropyl alcohol, diethyl ether, and 30% hydrogen peroxide (Baker and Adamson); ethyl alcohol (commercial solvents); and 72% $HClO_4$ (G. F. Smith). $LiClO_4$ was made by the neutralization of $LiOH \cdot H_2O$ (G. F. Smith) with $HClO_4$. The resulting solid was twice recrystallized from water. D_2O and cation-exchange resins were obtained from Bio-Rad Laboratories.

tert-Butyl hydroperoxide (Lucidol Corp., 90%) was vacuum distilled until an assay[13] of 99% peroxide was obtained, bp 37–38° (16 mm).

Cr(II) perchlorate solutions were prepared by the reduction of the Cr(III) salt with amalgamated zinc under a stream of nitrogen.[14] The solutions were analyzed for Cr(III) by measuring the absorbance at 408 nm. Stock solutions were made up fresh daily and the hydrogen peroxide was added to the substrate solutions just prior to each experiment. Ionic strength in all experiments was maintained with $LiClO_4$ and $HClO_4$. The acidity was fixed with $HClO_4$.

Kinetic Measurements and Analysis. Kinetic experiments were carried out with a Cary Model 14 spectrophotometer. The reactants were mixed by injecting through a rubber serum cap one reactant solution, which had been previously thermostated, into a cell containing the other thermostated reactant solution. Temperature control was $\pm0.2°$. The order of mixing the hydrogen peroxide–organic substrate solution and the Cr(II) solution had no effect on the kinetic behavior of the system. The solution containing hydrogen peroxide was always transferred using glass pipets or Teflon syringes. In the experiments reported, the Cr(II) solution was added to the hydrogen peroxide–organic substrate solution. Before mixing, all solutions were deoxygenated by passing a stream of nitrogen through the solution for at least 10 min. Cr(III) products were analyzed by spectrophotometry ($Cr(H_2O)_6^{3+}$, ϵ_{409} 15.6 and ϵ_{574} 13.4)[15] and/or by using a cation-exchange column for separation and characterization. On a Dowex 50-X8 column 0.7 M $HClO_4$ or 0.8 M $NaClO_4$ removes chromium species of charge 2+.

The product, CrL^{2+}, obtained from the reaction of Cr^{2+} with H_2O_2 and diethyl ether was stable enough for ion-exchange separation, and its absorption spectrum could be determined without needing to rely on assumptions as to the quantitative course of the reactions producing the ion. The total chromium content of the sample eluted from the cation-exchange column was determined using H_2O_2 in base as oxidant and measuring chromium as chromate ion (CrO_4^{2-}, ϵ_{372} 4815).[16]

For the systems with alcohol as substrate, the chromium complexes are too labile for quantitative isolation by an ion-exchange method. According to the mechanism[17] proposed for the reaction of Cr^{2+} with H_2O_2, HO is formed as follows.

$$H_2O_2 + Cr^{2+} \longrightarrow Cr^{3+} + HO + H_2O \tag{4}$$
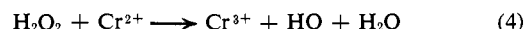
Hydroxyl radicals can react with substrate, forming an organic radical[18] (the desired reaction), or with Cr^{2+} or H_2O_2. To maximize the yield of complex dilute solutions were used (this tends to minimize reactions such as dimerization of radicals), alcohol was used well in excess of Cr^{2+}, and this in turn was used well in excess over H_2O_2 (*cf.* footnotes to Tables I and II). In one case, using isopropyl alcohol as substrate, a systematic study of the absorption of the Cr(III) complexes as a function of $[Cr^{2+}]/[alcohol]$ was carried out. As this ratio decreases, HO tends to be scavenged by alcohol rather than Cr^{2+}. The extinction coefficient obtained at 390 nm for the Cr(III) complex was estimated as 420 $\pm$ 40 M^{-1} cm^{-1}. This agrees rather well with that measured directly for the Cr(III) complex derived from diethyl ether, 360 M^{-1} cm^{-1}, and the agreement suggests that except for Cr^{2+} intercepting a small fraction of the hydroxyl radicals, formation of Cr(III) complexes in the systems is efficient.

The possibility of dimerization being a major reaction path for the radicals formed was investigated with isopropyl alcohol and *tert*-

(13) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, 19, 976 (1947).
(14) H. Taube and H. Myers, *J. Amer. Chem. Soc.*, 76, 2103 (1954).
(15) J. A. Laswick and R. A. Plane, *ibid.*, 81, 3564 (1959).
(16) G. W. Haup, *J. Res. Nat. Bur. Stand.*, 48, 414 (1952).
(17) L. B. Anderson and R. A. Plane, *Inorg. Chem.*, 3, 1470 (1964).
(18) An intermediate in the reaction of Ti^{3+} with H_2O_2 is known to extract H· from aliphatic alcohols with the β carbon being more reactive than the α carbon: N. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

butyl hydroperoxide (methyl radicals). In the case of the isopropyl radical, the dimer, pinacol, is a solid at room temperature (mp 38°). Reaction solutions for this system were evaporated to dryness and the residue was analyzed for pinacol. The dimerization product from the methyl radicals, ethane, was analyzed for by mass spectrophotometry. A spectrophotometric method[19] was used in the analysis of formaldehyde. In the methanol analysis,[20] the CH_3OH is first oxidized to HCHO with permanganate after which the HCHO concentration is determined in a manner similar to that described in ref 19.

Kinetics were followed at three wavelengths between 370 and 430 nm and found to be independent of wavelength. All experiments reported here were carried out at 410 nm. For the aquation of the chromium(III)–carbon species, rate constants, k, are defined by the relation

$$-d \ln [CrL^{2+}]/dt = k_1 + k_2[H^+] = k_{obsd}$$

The values of k_{obsd} were determined from plots of $\ln (A_t - A_\infty)$ vs. time for the data obtained under pseudo-first-order conditions. A_∞ and A_t are the absorbance at infinite time and time t.

Results

The Formation of CrL^{2+} Induced by the Reaction of Cr(II) with Hydrogen Peroxide.

The general experimental procedure was to add a solution of Cr(II) perchlorate to a solution containing the substrate (an alcohol or diethyl ether) and hydrogen peroxide. Neither the peroxide nor the Cr(II) reacts directly with the substrates under the experimental conditions. The product solutions were yellow and showed a visible spectrum with strong absorptions at ~390 nm. No dimerization product was found under the conditions of high dilution, and it is assumed that if any was formed it accounted for less than 5% of the organic radicals. This is in line with the findings of Kochi and Mocadlo[8a] in their work with methyl and ethyl radicals produced in the reduction of hydroperoxides. Of the complexes derived from the series of alcohols studied, that formed from methyl alcohol was the least labile and could be eluted from a cold cation-exchange column with 0.80 N NaClO$_4$, behavior which indicates a 2+ charge for the complex.

Since many of the chromium complexes were too labile for isolation, the aquation reactions were followed in the reaction mixture. It was necessary, therefore, to determine if excess Cr(II) affected the rate of aquation. The influence of Cr(II) was investigated by varying the concentration of Cr(II) while keeping all other reagents constant. The observed first-order rate constant for aquation of the isopropyl alcohol–chromium ion at 20° was the same, 5.6 × 10⁻³ sec⁻¹, in both 0.05 and 0.025 M Cr(II). The initial concentrations of the other reactants were [H₂O₂] = 4.4 × 10⁻³ M, [isopropyl alcohol] = 0.5 M, and [H⁺] = 0.54 M. It should be noted that Anet[3] found Cr(II) catalysis of the aquation of the benzylchromium ion when halide ions were present in the solution.

The mixture resulting from the reaction of Cr(II), hydrogen peroxide, and methyl alcohol was analyzed to determine if a significant amount of the organic radicals formed in the hydrogen abstraction step is further oxidized rather than being captured by a Cr(II) ion. Cr(II) was brought into reaction with H₂O₂, 2 mol:1 mol, in the presence of an excess of methyl alcohol at two different acidities, 0.10 and 1.0 M. The solutions were immediately placed on a cold cation-

(19) C. E. Bricker and H. R. Johnson, Anal. Chem., 17, 400 (1945).
(20) R. N. Boos, ibid., 20, 964 (1948).

exchange column which was then washed several times. The total eluent was analyzed for formaldehyde. The amount of HCHO found was essentially independent of the acid concentration and was ~0.5% of the initial chromium concentration. In another experiment in which Cr²⁺ reacted with H₂O₂, again in the ratio 2:1, in the presence of an excess of CH₃OH, the solution was placed on a cold cation-exchange column in a nitrogen atmosphere, and the chromium complex was eluted with a 1 M solution (0.9 M NaClO₄ and 0.1 M HClO₄). The eluent containing the chromium complex was divided into two aliquots, identical except in their acid concentration, which was adjusted to 0.10 M in one and 1.0 M in the other. After ~10 half-lives, the samples were analyzed for total chromium, CH₃OH, and HCHO. The results gave a ratio of chromium: CH₃OH:HCHO of 1:1.30:0.08 for the aquation in 1.0 M HClO₄ and 1:1.41:0.07 for the aquation in 0.10 M HClO₄. That the ratio of CH₃OH to chromium is greater than one is attributed to aquation occurring on the column during the ion exchange. The chromium product, $Cr(H_2O)_6{}^{3+}$, would remain on the column, while the ligand, CH₃OH, would wash through with the eluting solution.

Pseudo-first-order kinetics were obtained for the aquation of the isopropyl alcohol–chromium ion under all the conditions of acidity, ionic strength, and temperature investigated. The first-order plots remained linear over the entire course of the reaction. Table I lists the rate constants for the aquation of the chro-

Table I. Kinetic Data on the Aquation of $[(H_2O)_5CrC(OH)(CH_3)_2]^{2+}$ [a]

[H⁺], M	$10^3 k_{obsd}$, sec⁻¹	Temp, °K
0.095	1.44	288.2
0.273	1.72	288.2
0.497	2.03	288.2
0.720	2.46	288.2
0.095	3.03	296.0
0.273	3.85	296.0
0.497	4.81	296.0
0.720	5.78	296.0
0.095	6.73	303.6
0.273	8.20	303.6
0.497	9.90	303.6
0.720	11.55	303.6
0.295	4.72	298.2
0.519	5.83	298.2
0.742	6.80	298.2

[a] $\mu = 1.11$ (LiClO₄–HClO₄), [H₂O₂]$_{initial}$ = 4.4 × 10⁻³ M, [Cr²⁺]$_{initial}$ = 0.05 M, [CH₃CH(OH)CH₃]$_{initial}$ = 0.5 M.

mium complex derived from isopropyl alcohol. The data fit the rate law

$$-d \ln [CrL^{2+}]/dt = k_1 + k_2[H^+]$$

where $10^3 k_1$ takes the values 1.30 ± 0.05, 2.6 ± 0.1, 3.3 ± 0.1, and 6.1 ± 0.2 sec⁻¹ at 288.2, 296.0, 298.2, and 303.6°K, respectively, and $10^3 k_2$ at the same four temperatures takes the values 1.5 ± 0.1, 4.4 ± 0.3, 4.7 ± 0.3, and 8.9 ± 0.6 M^{-1} sec⁻¹. These data lead to values of $\Delta H^{\ddagger}{}_1$ and $\Delta S^{\ddagger}{}_1$ of 17.1 ± 0.7 kcal/mol and −11 ± 2 eu, and to $\Delta H^{\ddagger}{}_2$ and $\Delta S^{\ddagger}{}_2$ of 19.4 ± 0.8 kcal/mol and −5 ± 2 eu.

Table II shows kinetic data from experiments identical with those described above but using methyl, ethyl, and
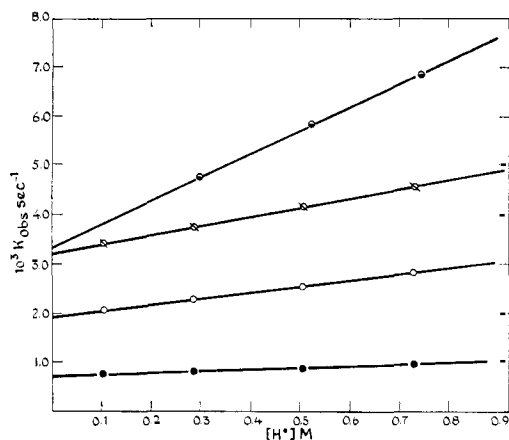
Figure 1. The observed rate constant for the aquation of penta-aquochromium(III) ions carbon bonded to aliphatic alcohols as a function of the hydrogen ion concentration; $\mu = 1.05$ (NaClO$_4$ + HClO$_4$): ●, isopropyl alcohol; ◔, n-propyl alcohol; O, ethyl alcohol; ●, methyl alcohol.

Figure 2. The molar absorbance of pentaaquo(diethyl ether)-chromium(III) ion; $\mu = 1.0$ (NaClO$_4$ + HClO$_4$).

n-propyl alcohols in place of isopropyl alcohol. These data were obtained at only one temperature, 298.2°K, but at several acidities. In the aquation reactions first-order kinetics were obtained for all three ligands with the first-order plots remaining linear over the entire course of the reaction. The rate is a function of the hydrogen ion concentration (Figure 1), and the kinetics again fit the two-term rate expression. At 298.2°K, $10^3 k_1$ takes the values 0.70 ± 0.02, 1.90 ± 0.05, and 3.2 ± 0.1 sec^{-1} for methyl, ethyl, and n-propyl alcohols, respectively, and $10^3 k_2$ for the same three ligands takes the values 0.32 ± 0.02, 1.22 ± 0.04, and 1.86 ± 0.06 M^{-1} sec^{-1}.

Table II. Kinetic Data on the Aquation of [(H$_2$O)$_5$CrL]$^{2+}$ (L = CH$_2$OH, CH$_3$CHOH, CH$_3$CH$_2$CHOH)[a]

L	[H$^+$], M	$10^3 k_{obsd}$, sec^{-1}
CH$_2$OH	0.104	0.75
	0.284	0.80
	0.506	0.86
	0.729	0.95
CH$_3$CHOH	0.104	2.06
	0.284	2.28
	0.506	2.54
	0.729	2.81
CH$_3$CH$_2$CHOH	0.104	3.40
	0.284	3.70
	0.506	4.13
	0.729	4.56

[a] $\mu = 1.05$ (LiClO$_4$–HClO$_4$), $T = 298.2$°K, [H$_2$O$_2$]$_{initial}$ = 4.4 × 10^{-3} M, [Cr^{2+}]$_{initial}$ = 0.03 M, [LH]$_{initial}$ = 0.5 M.

Thus far the details of the observations with alcohols as substrates have been emphasized, and we turn now to considering diethyl ether as substrate. It has been noted that when Ti^{3+} reacts with H$_2$O$_2$ in the presence of diethyl ether, hydrogen abstraction occurs primarily at the carbon adjacent to the oxygen atom.[21] Using experimental conditions similar to those used in the experiments with the alcohols (CH$_3$CH$_2$OCH$_2$CH$_3$ in excess of Cr(II), which in turn is in excess of H$_2$O$_2$), it was found that on mixing the three reactants a yellowish

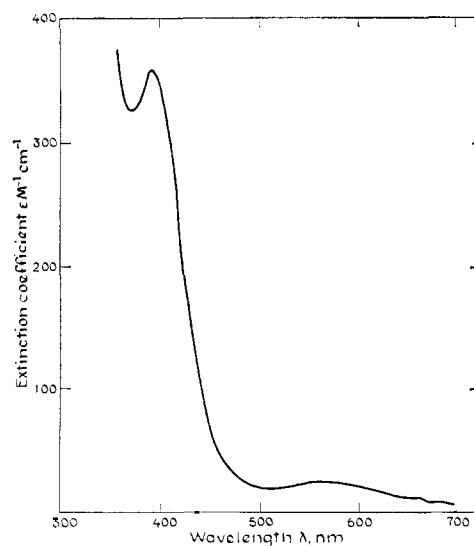(21) W. T. Dixon, R. O. C. Norman, and A. L. Baley, J. Chem. Soc., 3625 (1964).

product was formed. As in the previous cases, this product has a strong absorption band at ~390 nm. One immediate qualitative observation was that the product is relatively stable compared to the chromium complexes referred to previously. It was easily separated by ion exchange on a cold (~10°), nitrogen flushed, cation-exchange column. The product was eluted with <1 M NaClO$_4$ (this suggests an ion of +2 charge), and it was therefore possible to get an absorption spectrum without interference from Cr(H$_2$O)$_6$$^{3+}$. The spectrum of the diethyl ether–chromium ion is shown in Figure 2. In the visible region there is a major absorption at 390 nm and a smaller absorption at 561 nm. Chromium analysis of the sample gave molar extinction coefficients of 360 M^{-1} cm^{-1} at 390 nm and 23 M^{-1} cm^{-1} at 561 nm for the pentaaquo(diethyl ether)-chromium(III). The value at 390 nm is a minimum value as any aquation would have led to a smaller absorption. The chromium-containing product of aquation, which is Cr(H$_2$O)$_6$$^{3+}$, has a molar extinction coefficient of <15 M^{-1} cm^{-1} at 390 nm. There has been some discussion[3,4] as to whether the chromium complexes containing a carbon-bound ligand have an absorption band in the region of 550–580 nm. This was difficult to determine with the other complexes dealt with here, even those that could be ion exchanged, because aquation produces Cr(H$_2$O)$_6$$^{3+}$. The position of the maximum for the diethyl ether–chromium complex (λ_{max} 561 nm) is far enough from that of Cr(H$_2$O)$_6$$^{3+}$ (λ_{max} 574 nm) that it appears to be an absorption of the chromium complex and not of the aquation product, Cr(H$_2$O)$_6$$^{3+}$.

Table III contains the kinetic data for the aquation of the diethyl ether–chromium complex. The data show that the rate of aquation is first order in hydrogen ion and is described by the rate expression

$$-d \ln [CrL^{2+}]/dt = k_2[H^+]$$

At 298.2°K, $10^5 k_2$ has a value of 3.8 ± 0.1 M^{-1} sec^{-1}; the upper limit on k_1 is 5 × 10^{-7} sec^{-1}.

Chromium(II) and tert-Butyl Hydroperoxide. In previous work on this reaction, Kochi and coworkers[22]

Table III. Kinetic Data on the Aquation of Methylchromium(III) and (Diethyl ether)chromium(III)[a]

No.[b]	[H⁺], M	$10^3 k_{obsd}$, sec⁻¹
1	0.104	0.55
2	0.284	1.53
3	0.506	2.55
4	0.729	3.77
5	0.104	0.004
6	0.284	0.011
7	0.506	0.019
8	0.729	0.027

[a] $T = 298.2°K$, $\mu = 1.05$ (LiClO₄ + HClO₄). [b] For runs 1–4, [(H₂O)₅CrCH₃²⁺], [Cr²⁺]ᵢₙᵢₜᵢₐₗ = 0.03 M, [(CH₃)₃CO₂H]ᵢₙᵢₜᵢₐₗ = 0.01 M; for run 5–8, [Cr²⁺]ᵢₙᵢₜᵢₐₗ = 0.03 M, [CH₃CH₂OCH₂CH₃]ᵢₙᵢₜᵢₐₗ = 0.4 M.

found *tert*-butyl alcohol, acetone, and CH₄ (the latter two in equimolar amounts) as products. The *tert*-butyl alcohol is taken as arising from the reduction by Cr²⁺ of the radical (CH₃)₃CO·, produced in the primary step, and acetone and CH₄ are taken as resulting from the fragmentation reaction, eq 3. The amount of fragmentation products ranged from 6 to 18%, depending on the order of mixing the reagents.[22] It was assumed that CH₃· is trapped by Cr(II) and that CH₄ arises by hydrolysis of this ion, but no direct evidence for the presumed intermediate, (H₂O)₅CrCH₃²⁺, was obtained. The reduction of *tert*-butyl hydroperoxide by Cr(II) has been repeated in the current study using an excess of Cr(II). Under these conditions, [*tert*-butyl hydroperoxide] = 0.01 M and [Cr²⁺] = 0.03 M, the characteristic yellow color of a chromium complex containing a chromium–carbon bond formed immediately, and the visible spectrum was very close to that of the previously described complexes (Figure 2) having a strong absorption at ~390–395 nm. As in the work of Kochi,[8] only trace amounts of the dimerization product (ethane) appeared. In one set of experiments, after the methyl–chromium complex was formed in normal water, D₂O was added so that the aquation took place in deuterium-enriched water. Mass spectrometric analysis of the methane produced in this reaction and comparison of the enrichment to that of the water gave a monodeuterated methane of ~55% of the enrichment of the water. Since the D₂O was added after the methylchromium ion was formed, the deuterated methane was most likely formed during the aquation of the complex (hydrogen exchange between methane and solvent does not occur under these conditions). Kochi[8] performed the entire experiment in D₂O and found greater than 90% monodeuterated methane. Table III lists pseudo-first-order rate constants which were obtained at different acidities for the aquation of the methylchromium ion. As in the work with the other chromium complexes, the first-order plots remained linear over the entire course of the reaction. The data show that the aquation of methylchromium ion has a rate that is first order in hydrogen ion and can be described by the rate expression

$$-d \ln [CrL^{2+}]/dt = k_2[H^+]$$

At 298.2°K, $10^3 k_2$ has a value of 5.2 ± 0.2 M^{-1} sec⁻¹; the upper limit on k_1 is 1 × 10⁻⁴ sec⁻¹.

(22) J. K. Kochi and F. F. Rust, *J. Amer. Chem. Soc.*, **84**, 1193 (1962).

Reactions of Chromium–Carbon Complexes with O₂, NO, and CO. Preliminary studies were carried out on the reactions between the diethyl ether–chromium complex and O₂, NO, CO, H₂O₂, and CO₂. Oxygen reacts rapidly with the complex yielding some acetaldehyde and hexaaquochromium(III). It is possible that the organic product from the oxidation of the complex is the hemiacetal, CH₃CH₂OCH(OH)CH₃, which in an acid solution decomposes to acetaldehyde and ethyl alcohol. Acetaldehyde was also detected when the ethanol–chromium(III) complex reacted with oxygen. This product could arise through acetal, CH₃CH(OH)₂, as an intermediate. These results are preliminary and a complete product analysis has not been made. The diethyl ether–chromium(III) complex reacts rapidly with NO, somewhat slower with H₂O₂, and slowly with CO, yielding as yet unidentified products. Carbon dioxide reacts at most only slowly with this complex. Further work in this area is in progress.

Discussion

Other work already referred to has shown that carbon radicals are trapped efficiently by Cr²⁺. The cation-exchange results obtained in the present work with oxygen-containing ligands show that the corresponding radicals are also efficiently trapped by Cr²⁺, but it does not necessarily follow from this evidence that the ligand is bound to the Cr(III) through a carbon–chromium bond. Although the hydroxyl radical abstracts hydrogen from the carbon, rearrangement could produce an oxy radical which is then attacked by Cr(II). However, other experimental evidence points to the establishment of a chromium–carbon bond in the complex. All of the Cr(III) products have spectra which have a strong absorption at ~390 nm, closely approaching those of the chromium products obtained in the reduction of aralkyl halides and chloroform. Those products, it has been concluded,[3,4] contain organic ligands bonded through carbon. If the alcohols were bonded through oxygen, it is very likely under the acidic conditions of these experiments that the oxygen would be protonated, and it is expected then that the spectrum of an alcohol so bound would approximate that of the pentaaquo-alcohol–chromium(III) ion. Both the position of the maximum absorption and the molar extinction coefficients of the maxima found in our experiments are quite different from those found by King[23,24] and coworkers for pentaaquochromium complexes containing bound methanol and ethanol (*e.g.*, Cr(OH₂)₅-OCH₂H₅³⁺, ε₅₇₇ 14.6 and ε₄₁₀ 16.8). In addition, the chromium products formed in our experiments aquate to the hexaaquochromium(III) ion approximately 200 to 1000 times (methyl[23] and ethyl[24] alcohol, respectively) as fast as those with the alcohol bonded through the oxygen. The chromium complex formed from the reaction with the methyl radical can only be bonded through a carbon atom, and the deuterated methane formed in the aquation of the complex indicates that the methyl anion was bound to the chromium. In the case of diethyl ether, while there is an oxygen available, a coordinate bond between the chromium and this ether oxygen linkage appears less likely than a bond with the carbon atom. Since the visible spectra of all

(23) J. C. Jayne and E. L. King, *ibid.*, **86**, 3989 (1964).
(24) D. W. Kemp and E. L. King, *ibid.*, **89**, 3435 (1967).

the Cr(III) products are very similar, it appears as if the product which is formed in all our experiments is a pentaaquochromium(III) complex having a carbon-bonded ligand in the remaining coordination position.

The primary aquation products of the complexes studied in acidic aqueous media (and nitrogen atmosphere) are hexaaquochromium(III) and the organic molecule in the same oxidation state as it was prior to being oxidized by the hydroxyl radical.

$$(H_2O)_5CrL^{2+} + H_3O^+ \longrightarrow (H_2O)_6Cr^{3+} + HL \qquad (5)$$
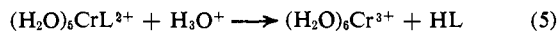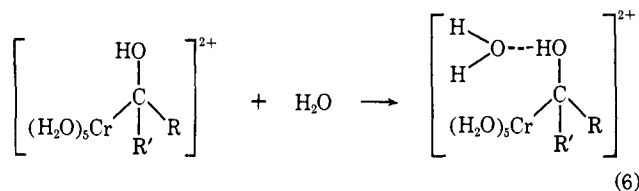
Table IV contains a summary of the rate data for the aquation of the complexes studied. It is interesting to note that all of the complexes which have a hydroxyl

Table IV. Summary of Rate Constants

Ligand	$10^3 k_1,^a$ sec^{-1}	$10^3 k_2,^a$ M^{-1} sec^{-1}	Temp, °K
CH$_3$C(OH)CH$_3$	6.1	8.9	303.6
CH$_3$C(OH)CH$_3$	3.3	4.7	298.2
CH$_3$C(OH)CH$_3$	2.6	4.4	296.0
CH$_3$C(OH)CH$_3$	1.3	1.5	288.2
CH$_3$OH	0.7	0.32	298.2
CH$_3$CHOH	1.9	1.22	298.2
CH$_3$CH$_2$CHOH	3.2	1.86	298.2
CH$_3$	<0.1	5.2	298.2
CH$_3$C(H)OC$_2$H$_5$	<0.0005	0.038	298.2

^{a} $k_{obsd} = k_1 + k_2[H^+]$.

function on the carbon atom bonded to the chromium aquate by two paths, of which one is zero order and the other first order in hydrogen ion concentration. The relatively low enthalpy of activation found for the acid-independent path of the isopropyl alcohol–chromium complex (~5–7 kcal lower than the enthalpies for the acid hydrolysis of most pentaaquochromium complexes with inorganic ligands[25]) suggests an activated complex in which the dissociation to products is "solvent assisted,"[26] or a dissociative mechanism of a complex having a weaker metal ligand bond. The fact that the diethyl ether– and methyl-chromium complexes do not have acid-independent paths for aquation, and the alcohol–chromium complexes do, suggests that a second body such as solvent participates in the activated complex. If the solvent does enter the activated complex, it would most likely be in a position so as to take advantage of hydrogen bonding[27] with the hydroxyl group of the alcohol. This would result in an activated complex of the type shown in
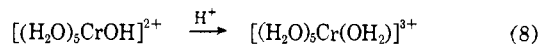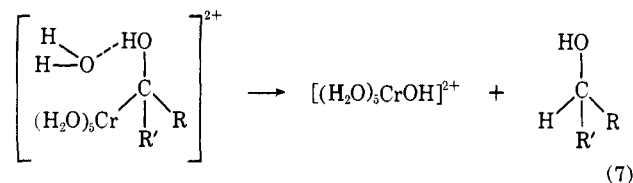

$$(6)$$

(25) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1965, pp 134 and 164.

(26) T. P. Jones, W. E. Harris, and W. J. Wallace, Can. J. Chem., 39, 2371 (1951).

(27) A. S. Adamson, J. Amer. Chem. Soc., 80, 3183 (1958).

which could then form the products

$$(7)$$

$$[(H_2O)_5CrOH]^{2+} \xrightarrow{H^+} [(H_2O)_5Cr(OH_2)]^{3+} \qquad (8)$$

The entropy for aquation of the isopropyl alcohol–chromium(III) ion is somewhat more negative than that found for many of the pentaaquochromium complexes. This may be due to the loss of freedom of movement of the solvent water molecule involved in the activated complex.[28] The activation parameters for the aquation of the isopropyl alcohol–chromium ion are close to those found by Kochi ($\Delta H^{\pm} = 16.2$ kcal/ mol and $\Delta S^{\pm} = -13.9$ eu) for the aquation of benzyl-chromium ion to toluene. However, under his conditions the anionic components of the buffer solution are involved in the reaction mechanism.

Under the acidic conditions of these experiments, it is not likely that aquation would produce a free carbanion, so it appears probable that a proton must be available in the activated complex prior to dissociation to the final products. While caution must be used in comparing rates without knowing activation energies, it is interesting to compare the hydrogen-ion-dependent rate constants (k_2) of aquation for the alcohols studied. The electron-donating or -withdrawing effect of the substituents on the chromium-bound carbon would suggest a reverse order from that actually found for the relative rate constants for aquation if the primary effect of the substituents was on the strength of the chromium carbon bond (i.e., primarily bond breaking). The ligands with electron-withdrawing substituents make the carbon more positive, which would result in a weaker bond to the chromium and would, therefore, be expected to lead to more facile hydrolysis. However, the opposite is noted, and it is the ligands with the electron-donating substituent which hydrolyze most readily. This would be consistent with a mechanism in which the products were Cr(II) and the free radical (which would then dimerize), but the enthalpy, the entropy, and the product analysis are not consistent with this path. The relative order of the aquation rates is consistent with a mechanism which requires a proton to be associated with the bound carbon so that on dissociation the organic product is a neutral molecule rather than a free carbanion (which would later protonate). The more negative the carbon, the more strongly would a proton be attracted to a site. The enthalpy for the hydrogen-ion-dependent path of the isopropyl alcohol–chromium ion is very close to that of the hydrogen-ion-independent path, suggesting a similar mechanism, that is, a solvent-assisted dissociation with the solvent molecule hydrogen bonded through the proton (see the reaction in eq 9 below). The slightly lower entropy for this path could be accounted for by the smaller change in charge density going from activated complex to products.

(28) H. R. Hunt and H. Taube, ibid., 80, 2642 (1958).

$$\longrightarrow [(H_2O)_5CrOH_2]^{3+} + $$

(9)
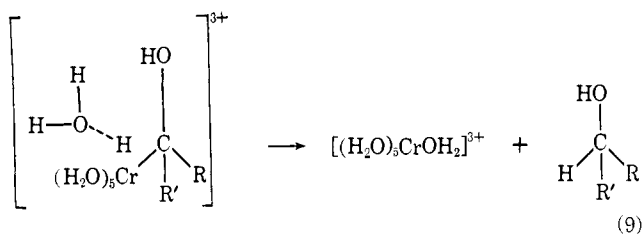
A similar mechanism appears reasonable for those ligands which contain no hydroxyl function. The kinetics for the chromium complexes containing these ligands have only one path and that is first order in hydrogen ion. If the activated complex involves a solvent molecule cis to the organic ligand, steric effects would be expected to be important. Thus, although the carbon in the methyl ligand is more positive than that of the alcohols, its rate constant for aquation, k_2, is larger. This may well be due to the ease with which a hydronium ion could approach the face of the octahedron on the side containing the methyl ligand. The relatively low amount of CH_3D ($\sim55\%$ of the D_2O concentration) found on aquation of the methylchromium ion would also be in the direction of the isotope effect expected for a path which involved the participation of a solvent molecule in the activated

complex. The relatively slow rate of hydrolysis of the diethyl ether ligand could be due primarily to steric effects. Not only are there no substituents (hydroxy groups) to assist a solvent molecule by hydrogen bonding, but the methyl group and the ethyl ester groups, not being strongly hydrophilic, would interfere with the approach of a solvent molecule.

The activation parameters found by Coombes and coworkers[7] ($\Delta H^{\neq}$'s 30-40 kcal/mol and generally positive $\Delta S^{\neq}$'s up to 37 eu) for the acid hydrolysis of the pentaaquo(pyridiomethyl)chromium(III) ions are significantly different from those found in the current study and those of Kochi and Buchanan.[5] However, their experiments were done in the presence of oxygen, and their primary product was a pyridine aldehyde. Based on our preliminary experiments with the carbon-bonded Cr(III) complexes and various oxidizing agents, it is quite probable that the reaction under these conditions is different from the aquation reaction observed in an oxygen-free environment.

Orbital Symmetry Restraints to Transition Metal Catalyzed [2 + 2] Cycloaddition Reactions

Frank D. Mango* and J. H. Schachtschneider

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Abstract: Suprafacial [2 + 2] cycloaddition reactions can be catalyzed by certain transition metal complexes. One mechanism for the process involves an exchange of electron pairs between the metal center and the transforming ligands. This process would effect a spatial redistribution of metal valence electrons within the complex which can introduce energy barriers due to the ligand field of the nonreacting ligands. These barriers can, conceivably, be significant, playing a dominant role in the chemistry of metal-catalyzed [2 + 2] valence isomerizations. Coordination geometries describing restrictive and nonrestrictive ligand fields are discussed. Metal complexes capable of coordination geometries of a nonrestrictive nature are suggested as models for catalytically active metal systems. Examples include metals capable of six- and seven-coordination of C_{2v} symmetry.

Orbital symmetry conservation places significant restraints on the modes of transformation open to organic molecules.[1] Certain transition metal complexes are known to dramatically catalyze symmetry-forbidden transformations,[2] and a mechanism involving

the removal of symmetry restrictions has been proposed.[3] Organic ligands coordinated to transition metal complexes, however, are not totally removed from symmetry restrictions; molecular transformations along certain modes of reaction can experience restraints due to the nature of the transforming ligands[4]

(1) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(2) (a) H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967); P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968); (b) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *ibid.*, **91**, 218 (1969); T. J. Katz and S. H. Cerefice, *Tetrahedron Lett.*, 2509, 2561 (1969); (c) G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968); M. Green and D. C. Wood, *Chem. Commun.*, 1062 (1967); *J. Chem. Soc.*, 1172 (1969); A. Greco, A. Carbonara, and G. Dall'Asta, *J. Org. Chem.*, **35**, 271 (1970); P. Heimbach and W. Brenner, *Angew. Chem., Int. Ed. Engl.*, **6**, 800 (1967); (d) R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 170 (1964); M. Calderon, E. A. Ofstead, J. P. Ward, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968); (e) H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 830 (1967); N. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788

(1967); (f) G. N. Schrauzer, R. K. Y. Ho, and G. Schlesinger, *Tetrahedron Lett.*, 543 (1970); (g) W. Reppe, O. Schlichting, K. Klager, and T. Towpel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948); G. N. Schrauzer, *Angew. Chem., Int. Ed. Engl.*, **3**, 185 (1964); (h) for a general discussion and review of some of this chemistry, see F. D. Mango, *Advan. Catal.*, **20**, 291 (1969).

(3) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); F. D. Mango, *Tetrahedron Lett.*, 4813 (1969); a forbidden-to-allowed description of the [1,3] suprafacial sigmatropic transformation has also been postulated[2h] and a similar treatment of disrotatory ring opening of cyclobutenes has been described.[2e,h]

(4) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **91**, 1030 (1969).